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Compositions for drying solid surfaces

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(56) Related Art
US 5346645
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A B S T R A C T

A drying composition according to the invention is composed of a solution of a surface-active agent in a mixture of a fluorinated hydrocarbon and of a polyfluorinated alcohol of formula:

$$Rf-(CH_2)_n-OH \qquad (I)$$

in which n is equal to 1 or 2 and Rf represents a linear perfluoroalkyl radical containing from 2 to 8 carbon atoms.

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Invention Title: COMPOSITIONS FOR DRYING SOLID SURFACES

The following statement is a full description of this invention, including the best method of performing it known to us :-

DESCRIPTION

The invention relates to the field of drying and the subject of the invention is more particularly compositions for removing the water which superficially wets solid surfaces, in particular electronic materials (printed or integrated circuits), precision mechanical components, glass substrates and military, aerospatial, aeronautical or medical equipment.

The usual process for dewetting solid surfaces consists in immersing the wet substrate in an organic solution of an ionic or non-ionic surface-active agent. Until recently, the organic solvent commonly used was 1,1,2-trichloro-1,2,2-trifluoroethane (CFC 113) but its use has been banned because of its harmful effect on the stratospheric ozone layer.

The use of 1-chloro-1,1-difluoroethane (HCFC 141b), provided as substitute for CFC 113 in dewetting compositions, is already regulated and before long it will no longer be possible to use this compound.

To replace CFC 113 and HCFC 141b, the use has been envisaged of fluorinated hydrocarbons which, like 1,1,1,3,3-pentafluorobutane (365 mfc), 1,1,1,2,2,4,4-heptafluorobutane (347 mcf), (perfluorobutyl)ethylene ($C_4F_9CH=CH_2$), 1H-perfluorohexane, n-perfluorohexane (PF 5060) or 1,1,1,2,3,4,4,5,5,5-decafluoropentane (43-10 mee), and perfluoro(methylmorpholine) (PF 5052), have no effect on the stratospheric ozone layer (zero

ODP), do not exhibit a flash point and, as is shown in the following table, possess physical characteristics which are similar to those of CFC 113 and HCFC 141b.

Solvent	Boiling point (°C)	Surface tension at 25°C (mN/m)	Relative density at 20°C
CFC 113	47.6	17.7	1.57
HCFC 141b	32	19.5	1.23
365 mfc	40	16.2	1.27
347 mcf	33.3	14.2	1.42
$C_4F_9CH=CH_2$	59	13.6	1.46
$C_6F_{13}H$	71	13	1.70
PF 5060	56	12	1.68
PF 5052	50	13	1.70
43-10 mee	54	14.1	1.58

However, the replacement of CFC 113 or of HCFC 141b by a fluorinated hydrocarbon such as those mentioned above is unsatisfactory because ionic-surface-active agents, which are most often used in dewetting compositions, are insoluble therein. Non-ionic surface-active agents are soluble in these fluorinated hydrocarbons but their dewetting effectiveness is often unsatisfactory.

To solve this problem in the case of 365 mfc, provision has been made, in the publication of Patent JP 05-168805, for the addition of a cosolvent chosen

from alcohols, ketones, alkanes and ethers. However, when the cosolvent is an alcohol comprising 1 to 3 carbon atoms, or a ketone, it is rapidly removed with the water, causing the rapid precipitation of the surface-active agent. As regards alkanes and ethers, they exhibit a flash point, which presents a safety problem for dewetting plants.

It has now been found that the use of tridecafluorooctanol ($C_6F_{13}CH_2CH_2OH$) and more generally of a water-immiscible polyfluorinated alcohol makes it possible to dissolve the majority of dewetting surface-active agents in fluorinated hydrocarbons without a harmful effect on the ozone layer.

The subject of the present invention is thus, as composition useful for the dewetting of solid surfaces, a solution of at least one surface-active agent in a mixture of at least one fluorinated solvent and of at least one polyfluorinated alcohol of general formula:

$$Rf-(CH_2)_n-OH \qquad (I)$$

in which n is equal to 1 or 2 and Rf represents a linear or branched perfluoroalkyl radical containing from 4 to 8 carbon atoms. Such a composition does not exhibit a flash point under the standard determination conditions (ASTM standard D 3828).

In accordance with the present invention, the fluorinated solvent, which is liquid at room temperature, must not contain halogen atoms other than

fluorine but it can contain heteroatoms, such as oxygen or nitrogen. Use is advantageously made of a fluorinated solvent with a normal boiling point of between 20 and 100°C, preferably between 30 and 75°C. Saturated or unsaturated fluorinated hydrocarbons containing from 3 to 6 carbon atoms, such as, for example, the compounds 365 mfc, 347 mcf, $C_4F_9CH=CH_2$, PF 5060 and 43-10 mee mentioned above, as well as 1H-perfluorohexane ($C_6F_{13}H$) and 1,1,1,2,2,3,3,4,4-nonafluorohexane, are particularly well suited.

The polyfluorinated alcohols of formula (I) are known products. Among these, it is preferable to use those in which n is equal to 2. A more particularly preferred polyfluorinated alcohol is tridecafluorooctanol ($C_6F_{13}CH_2CH_2OH$ hereinafter TDFO).

The amount of polyfluorinated alcohol necessary to completely dissolve the surface-active agent in the dewetting composition according to the invention can vary within wide limits, depending on the nature of the fluorinated solvent and of the surface-active agent employed and according to the desired concentration of surface-active agent. For a normal concentration of surface-active agent (0.01 to 0.5% by weight), a content of polyfluorinated alcohol ranging up to 30% by weight is generally sufficient to produce complete dissolution of the surface-active agent; in certain cases, even a very low proportion of polyfluorinated alcohol (0.1%) proves to be sufficient.

Consequently, in the dewetting composition according to the invention, the content of polyfluorinated alcohol can range from 0.1 to 30% by weight but it is advantageously between 0.5 and 5%.

In the composition according to the invention, the surface-active agent can be any surface-active agent commonly used in dewetting compositions. Thus, non-ionic surface-active agents, such as fatty esters (for example, caprylamine caprylate and caprylamine, dodecylamine or stearylamine caproate), or fluorinated non-ionic surface-active agents, such as, for example, adducts of ethylene oxide with a polyfluorinated alcohol of formula (I), esters of polyfluorocarboxylic acids, (polyfluoroalkyl)aminoalcohols, polyfluoroalkyl sulphides or polysulphides, or polyfluoroalkanecarbonamides or -sulphonamides, can be used. It is also possible to use anionic surface-active agents (for example a polyfluorosulphonic acid) but it is preferable to use cationic surface-active agents and more particularly those obtained by reaction of a mono- or dialkyl phosphoric acid of general formula:

$$(RO)_p(HO)_{2-p}PO_2H \qquad (II)$$

in which p is a number ranging from 1 to 2 and R denotes a linear or branched alkyl radical containing from 1 to 18 carbon atoms, with a quaternary ammonium chloride of general formula:

$$R'_2N^+R''_2\ Cl^- \qquad (III)$$

in which R' and R", which are identical or different, each represent a hydrogen atom or an alkyl or hydroxyalkyl radical containing 1 to 4 carbon atoms, and a fluorinated amine of general formula:

$$R_F\text{-}X\text{-}NR^1R^2 \qquad (IV)$$

in which R_F represents a linear perfluoroalkyl radical containing from 2 to 20 carbon atoms, X represents a divalent bridge and the symbols R^1 and R^2, which are identical or different, each represent a hydrogen atom or an alkyl or hydroxyalkyl radical containing 1 to 4 carbon atoms.

Such cationic surface-active agents and their preparation are described in Patents FR 2,522,007 and 2,691,473, the contents of which are incorporated here by reference. As in the abovementioned patents, it is preferable to use:

- acids (II) in which R is a butyl, hexyl, 2-ethylhexyl, octyl or tridecyl radical and more particularly mixtures of monoalkyl phosphoric acid and of dialkyl phosphoric acid in which the proportion by weight of the two acids is between approximately 60/40 and 40/60,

- quaternary ammonium chlorides (III) in which R' is a dodecyl or octadecyl radical and R" is a methyl radical or the commercial products mostly containing these chlorides,

- fluorinated amines of formula:

$$R_FC_2H_4SO_2NHCH_2CH_2CH_2N(CH_3)_2$$

or

$$R_FC_2H_4CONHCH_2CH_2CH_2N(CH_3)_2$$

As in the compositions of the prior art, the content of surface-active agent(s) in the dewetting composition according to the invention can vary within wide limits. This content is generally low (from 0.01 to 0.5% by weight, preferably 0.04 to 0.2%) in ready-for-use dewetting compositions but it can reach up to 30% by weight in concentrated compositions which only have to be diluted for the dewetting operation.

The solid surfaces from which water can be removed by means of a composition according to the invention can be highly varied, provided, however, that their substance (glass, metal, refractory material, plastic, and the like) is insoluble in and cannot be attacked by the fluorinated solvent(s) of the composition according to the invention.

The following examples illustrate the invention without limiting it. The cationic surface-active agents SA1 and SA2 were prepared from the following commercial products:

- <u>butyl phosphoric acid</u> $(C_4H_9O)_{1.5}(OH)_{0.5}PO_2H$ exhibiting the following acid values:

strong acidity: 0.566 equivalent per 100 g

weak acidity: 0.276 equivalent per 100 g

which corresponds to a mixture containing approximately 40% of monobutyl phosphoric acid and 60% of dibutyl phosphoric acid.

- Noramium M2C: mixture of different homologues of formula:

$$R'_2N^+CH_3)_2\ Cl^-$$

in which the distribution of the fatty chains (R') is as follows:

C_8	3%
C_{10}	6%
C_{12}	56%
C_{14}	18%
C_{16}	10%
C_{18}, saturated	2%
C_{18}, unsaturated	5%

This commercial product contains 75% of active material and contains 0.161 chloride equivalent per 100 g.

Preparation of the surface-active agent SA1

2.69 g of butyl phosphoric acid, 3.91 g (i.e. 7.6 meq.) of the fluorinated amine $C_6F_{13}C_2H_4SO_2NHCH_2CH_2CH_{2N}(CH_3)_2$, 3 g of a 10% methanolic sodium hydroxide solution (i.e. 7.6 meq. NaOH) and 8.32 g of Noramium M2C are added successively and with stirring to 150 g of HCFC 141b. This final addition causes the immediate formation of a sodium chloride precipitate which is removed by filtration (weight of NaCl collected: 0.4 g).

After removing the sodium chloride precipitate, the filtrate is then evaporated to dryness at 110°C in an oven. 14.8 g of surface-active agent SA1 are thus obtained.

Preparation of the surface-active agent SA2

The preparation is carried out as above but replacing the 150 g of HCFC 141b with 300 g of TDFO and dispensing with the final stage of evaporation to dryness. A solution containing approximately 5% of surface-active agent SA2 in TDFO is thus obtained.

EXAMPLE 1

A dewetting solution is prepared by dissolving 100 mg of surface-active agent SA1 in a mixture of 95 g of HFC 365 mfc and 5 g of TDFO and then this solution is introduced into a beaker placed in a small Branson 2200 ultrasonic vessel.

A 20 × 50 mm stainless steel grid, wetted beforehand by immersion in water, is then immersed in the dewetting solution and maintained under ultrasonic agitation for one minute.

After having been withdrawn from the dewetting solution, the grid is immersed in absolute alcohol and the quantitative determination of water by the Karl Fischer method indicates that 94% of the water has been removed.

The same result is obtained if the fluorinated alcohol TDFO is replaced with the same amount of a technical mixture of alcohols of formula $Rf\text{-}CH_2CH_2\text{-}OH$, the distribution of the Rf radicals being centred about C_6.

If the fluorinated alcohol TDFO is replaced with the same amount of n-pentanol or of n-hexanol, the

degree of removal of the water is only 60% and 72% respectively.

EXAMPLE 2

A dewetting solution is prepared by mixing 1 g of the solution containing 5% of surface-active agent SA2 and 99 g of HFC 365 mfc. A dewetting solution containing 500 ppm of surface-active agent SA2 is thus obtained, which solution is used as in Example 1. The degree of removal of the water is 95%.

Substantially the same result is obtained by using a dewetting solution containing 0.1% of surface-active agent SA2 in a mixture of 99 g of HFC 365 mfc and 1 g of TDFO.

EXAMPLES 3 to 11

The procedure is as in Example 2, but replacing the solvent HFC 365 mfc with other fluorinated solvents. The operating conditions and the results are combined in the following table.

Example	Solvent	(%)	% of TDFO	SA2 (ppm)	Water removed (%)
3	347 mcf	98	2	500	93
4	$C_4F_9CH=CH_2$	95	5	1000	92
5	$C_4F_9CH=CH_2$	99	1	500	95
6	$C_4F_9CH_2CH_3$	99	1	500	91
7	$C_4F_9CH_2CH_3$	98	2	500	92
8	$C_6F_{13}H$	98	2	500	91
9	PF 5060	99	1	500	92
10	PF 5052	99	1	500	94
11	43-10 mee	98	2	500	94

EXAMPLE 12

The procedure is as in Example 1, but replacing the fluorinated alcohol TDFO with pentafluoropropanol ($CF_3CF_2CH_2OH$, hereinafter PFP) and using a dewetting solution obtained by dissolving 100 mg of surface-active agent SA1 in a mixture of 80 g of HFC 365 mfc and 20 g of PFP. The degree of removal of the water is 95%.

EXAMPLE 13

The procedure is as in Example 1, but using a dewetting solution obtained by dissolving 100 mg of N,N'-dioleoyl-N-oleylpropylenediamine (hereinafter surfactant SA3) in a mixture of 90 g of HFC 365 mfc and

10 g of TDFO. The degree of removal of the water is 91%.

If the TDFO is replaced with the same amount (10 g) of PFP, the degree of removal of the water is 93%.

EXAMPLE 14

The procedure is as in Example 1, but using a dewetting solution obtained by dissolving 100 mg of the adduct of 6 mol of ethylene oxide with one mole of TDFO in a mixture of 99 g of HFC 365 mfc and 1 g of TDFO. The degree of removal of the water is 90%.

If the mixture of 365 mfc and of TDFO is replaced with a mixture of 90 g of 365 mfc and 10 g of PFP, the degree of removal of the water is also 90%.

EXAMPLES 15 to 18

The procedure is as in Example 1, but replacing the fluorinated alcohol TDFO with PFP and using a dewetting solution obtained by dissolving, in a mixture of 80 g of HFC 365 mfc and 20 g of fluorinated alcohol PFP, 100 mg of one of the following surface-active agents:

SA4 = $C_6F_{13}C_2H_4(OC_2H_4)_6OH$

SA5 = $C_8F_{17}C_2H_4N(C_2H_4OH)_2$

SA6 = $C_6F_{13}C_2H_4SO_2NHCH_2CH_2CH_2N(CH_3)_2$

SA7 = $C_6F_{13}C_2H_4SO_3H$, $H_2NCH_2CH(C_2H_5)C_4H_9$

The results obtained are combined in the following table.

Example	Surface-active agent	Water removed (%)
15	SA4	93
16	SA5	93
17	SA6	93
18	SA7	95

EXAMPLE 19

22 litres of the dewetting solution of Example 2 are charged to the dewetting and settling tanks of a drying machine with a capacity of 33 litres and 11 litres of pure HFC 365 mfc are charged to the rinsing vessel.

A wet stainless steel grid, resulting from a prior washing and rinsing treatment in aqueous medium, is immersed in the dewetting tank for 3 minutes and then rinsed for 3 minutes in the pure HFC 365 mfc at boiling point.

The drying performance was evaluated in the following way:

The grid is subsequently immersed in 100 g of absolute ethanol, the water content of which was determined beforehand by the Karl Fischer method. A new quantitative determination carried out after immersion of the grid revealed no increase in the water content, which means that the composition according to the invention makes it possible to obtain virtually complete removal of the water.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. Dewetting composition, characterised in that it is composed of a solution of at least one surface-active agent in a mixture of at least one fluorinated solvent and of at least one polyfluorinated alcohol of general formula:

$$Rf\text{-}(CH_2)_n\text{-}OH \qquad (I)$$

in which n is equal to 1 or 2 and Rf represents a linear or branched perfluoroalkyl radical containing from 4 to 8 carbon atoms.

2. Composition according to claim 1, containing at least one alcohol of formula (I) in which n is equal to 2.

3. Composition according to claim 1, in which the alcohol of formula (I) is tridecafluorooctanol ($C_6F_{13}CH_2CH_2OH$).

4. Composition according to any one of claims 1 to 3, in which the fluorinated solvent has a normal boiling point of between 20 and 100°C, preferably between 30 and 75°C.

5. Composition according to claim 4, in which the fluorinated solvent is a saturated or unsaturated fluorinated hydrocarbon containing from 3 to 6 carbon atoms.

6. Composition according to claim 4 or 5, in which the fluorinated hydrocarbon is chosen from 1,1,1,3,3-pentafluorobutane, 1,1,1,2,2,4,4-heptafluorobutane, 1,1,1,2,3,4,4,5,5,5-decafluoropentane, 1,1,1,2,2,3,3,4,4-nonafluorohexane, 1H-perfluorohexane, n-perfluorohexane, (perfluorobutyl)ethylene and perfluoro(methylmorpholine).

7. Composition according to any one of claims 1 to 6, in which the surface-active agent is a cationic surface-active agent obtained by reaction of a mono- or dialkyl phosphoric acid of general formula:

$$(RO)_p(HO)_{2-p}PO_2H \qquad (II)$$

in which p is a number ranging from 1 to 2 and R denotes a linear or branched alkyl radical containing from 1 to 18 carbon atoms, with a quaternary ammonium chloride of general formula:

$$R'_2N^+R''_2\,Cl^- \qquad (III)$$

in which R' and R", which are identical or different, each represent a hydrogen atom or an alkyl or hydroxyalkyl radical containing 1 to 4 carbon atoms, and a fluorinated amine of general formula:

$$R_F\text{-}X\text{-}NR^1R^2 \qquad (IV)$$

in which R_F represents a linear perfluoroalkyl radical containing from 2 to 20 carbon atoms, X represents a divalent bridge and the symbols R^1 and R^2, which are identical or different, each represent a hydrogen atom or an alkyl or hydroxyalkyl radical containing 1 to 4 carbon atoms.

8. Composition according to claim 7, in which R is a butyl, hexyl, 2-ethylhexyl, octyl or tridecyl radical, R' is a dodecyl or octadecyl radical, R" is a methyl radical, X is a $-CH_2CH_2SO_2NHCH_2CH_2CH_2-$ or $-C_2H_4CONHCH_2CH_2CH_2-$ bridge and R^1 and R^2 are methyl radicals.

9. Composition according to any one of claims 1 to 8, in which the content of polyfluorinated alcohol(s) is between 0.1 and 30% by weight, preferably between 0.5 and 5%.

10. Composition according to any one of claims 1 to 9, in which the content of surface-active agent(s) is between 0.01 and 0.5% by weight, preferably between 0.04 and 0.2%.

11. Composition according to any one of claims 1 to 9, in the form of a concentrate containing up to 30% by weight of surface-active agent(s).

12. Use of a composition according to any one of claims 1 to 10 for the dewetting of solid surfaces.

DATED this 5th day of February 2001

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LCG:KMH:VRH P10123AU00

BM

- (G) WPI / DERWENT
AN - 1980-83722C [47]
PR - JP19790039208 19790330
TI - Working fluid for Rankine cycle - comprises greater than one poly:fluoro-organic cpd.
IW - WORK FLUID RANKINE CYCLE COMPRISE GREATER ONE POLY FLUORO ORGANIC COMPOUND
PA - (DAIK) DAIKIN KOGYO KK
PN - JP55131096 A 19801011 DW198047 000pp
- JP61026832B B 19860623 DW198629 000pp
IC - C09K5/00 ; C10M3/24 ; F01K25/00
AB - J55131096 Working fluid comprises >=1 polyfluoroorganic cpd. selected from perfluorobutane, 1-hydro-heptafluoropropane, 1,4-dihydro-octafluorobutane, 1-hydro-nonafluorobutane, n-perfluoropentane, iso-perfluoropentane, neo-perfluoropentane, perfluorodimethylethylamine, perfluoromethyldiethylamine, perfluoro-1,3-dimethylcyclobutane, n-perfluorohexane, perfluorodipropylether, iso-perfluorohexane, perfluoro-N-methylmorpholine, 1-chloro-4-hydrooctafluorobutane, 1,4-dichloro-1-hydro-heptafluorobutane, perflurocyclohexane, perfluoro-2-methyl-tetrahydropyrane, 2,5-dihydro-perfluorohexane, perfluorotriethylamine, 1-hydro-perfluorohexane, 1,6-dihydroperfluorohexane, perfluoro-n-heptane, perflurodiethylpropylamine, and/or 2-chloro-5-hydro-perfluorohexane.
- The working fluid is most suitable fluid for a Rankine cycle system because its specific heat is greater thus the expander output is greater and because the fluid is less in combustable than usual hydrocarbons, less toxic and has high heat stability.